

Technique for Manufacture of Chlorotris(triphenylphosphine)rhodium(I)

The invention has to do with a technique for the manufacture of
5 chlorotris(triphenylphosphine)rhodium(I). This compound became known as
“Wilkinson’s Catalyst” and is utilized in numerous industrial processes, mainly
hydrogenations and hydroformylations. The most familiar method for the manufacture
of them stems from Sir Geoffrey Wilkinson and has found its way into the standard
reference work “Inorganic Syntheses” [Inorg. Synth **10**, 67 (1967) and identically
10 Inorg. Synth **28**, 77 (1990)]. According to this technique RhCl_3 -hydrate is made to
react with excess triphenylphosphine in ethanol and the compound is obtained in a
yield of 88% relating to the rhodium used.

It has now been discovered that the technique can be decisively improved both in
15 terms of the product’s yield as well as in terms of quality. Surprisingly during the
reaction temperature control directly and demonstrably impacts the product’s quality.

With large-scale manufacture of Wilkinson’s Catalyst the determining factor is that a
crystalline product be obtained that is well filterable. In this respect crystals too small
20 are not useful because they clog filtering devices, such as filters, Filter funnels or frits,
or the filters cannot retain the crystals. It has been discovered that the size of the
crystal is surprisingly adjustable by means of temperature and solvents.

The invention thus has to do with a technique for the manufacture of chlorotris(tri-
25 phenylphosphine)rhodium(I) by reaction of a RhCl_3 solution with triphenylphosphin
in mixtures of a C_2 - C_5 alcohol with water, subsequent cooling and filtering of the
crystalline precipitate obtained whereby the mixture of the reactants is handled in
such a way that

- A in an initial stage is heated up to about 30°C ,
- 30 B later in a second stage is heated up from 30 to about 75°C ,
- C is maintained at 80 to 110°C .

In so doing Stage A can be eliminated if the mixture is already 30°C warm or warmer (cf. Embodiment 1). Stages A and B can even merge if for somewhat more than a time period of 3/2 to several hours it is heated up from room temperature (cf.

Embodiment 3). As can be seen from the embodiments the temperature indication of
 5 “about 30°C” is relating to a temperature range of 25 to 35°C. Also the indication of
 “about 75°C” refers to a temperature range that lies between 68 and 79°C and in
 which with the inventive technique the point of change into a deep dark red solution
 normally lies, showing the reaction has taken place completely. Further, with the use
 of ethanol as a solvent the lower temperature limit at step C is to be lowered to 78°C.

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Preferably the duration of the individual stages amounts to: A about ½ - 1 h, B about
 1 - 4 h and C about ½ - 1 h. Here the limits are to be taken loosely, that means, e.g.,
 +/- 10 minutes with a half hour and +/- 30 minutes with 4 hours. However an effort is
 made for economic reasons not to design the duration of the stages too long.

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Particularly beneficial is a technique for the manufacture of chlorotris(tri-
 phenylphosphine)rhodium(I), by which

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- a solution of RhCl_3 is manufactured in water or a RhCl_3 solution is prepared
 from a recycling process.
- the solution is combined with a C_2 - C_5 -alcohol combined, preferably
 isopropanol, if need be in a protective inert gas and/or under cooling (e.g. in
 an ice bath),
- triphenylphosphine is added in excess, if need be as alcohol solution or
 25 suspension, if need be again under cooling.

A the mixture or suspension obtained is heated up in an initial stage from
 about 5 to 20 to about 30°C,

B later in a second stage is heated up from about 30 up to about 75°C,

C maintained at 80 to 110°C or, if need be, boiled under reflux,

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- the solution obtained is cooled down,

- the crystals precipitated out are filtered, washed with alcohol and/or water and/or petroleum ether and subsequently dried.

Preferably at Step B the heat-up is done slowly in such a way that the solution's color change to dark red takes place at the highest possible temperature, by preference at about 75°C. This change indicates the reaction to chlorotris(triphenylphosphine)rhodium(I) that later is obtained as dark red crystals. On fast heat-up of the suspension in Step B the dark red color change already occurs at about 60°C. Later upon cool down such small crystals arise that the filtration appliances, such as frits, clog or the filter is not able to retain the crystals. If the temperature is controlled in such way that at first it is heated up for some time (with starting points in the 100 g range ½ h) from room temperature (18 to 20°C) to about 30°C, then in an additional phase about 3 h. long is heated up from about 30 to 75°C, the color change first takes place at about 75°C. The resulting crystals are demonstrably adequate in size to be smoothly filtered and also meet catalyst users' requirements and specifications.

In a preferred embodiment of the technique the RhCl_3 is used in the form of an aqueous solution from a recycling process. Surprisingly this has an impact on the quality of the crystals obtained. At the same time the determining factor appears to be the role of water. Triphenylphosphine dissolves in isopropanol but is almost insoluble in water. By the thinning effect upon addition of about a 10% aqueous RhCl_3 solution the solubility of triphenylphosphine is reduced. This is represented in Embodiment 3, according to which a good yield of well filterable, specification-adjusted crystals is manufactured.

Alternatively thereto it can prove to be advantageous not to dissolve the triphenylphosphine in alcohol completely, but rather to use it as an alcoholic suspension. Triphenylphosphine does not dissolve in particular at low temperatures completely right away, but rather first starts dissolving slowly with rising temperature and is only then available for the reaction with RhCl_3 . According to this effect the mole ratio between RhCl_3 and triphenylphosphine is different from the quantities introduced, and even here the crystal size is again surprisingly favorably impacted by the initial lack of triphenylphosphine.

The invention thus also has to do with a technique for the manufacture of cholotris(triphenylphosphine)rhodium(I), with which

- 5 - a RhCl_3 solution is manufactured in water or a RhCl_3 solution is prepared from a recycling process,
- isopropanol is produced under an inert protective gas,
- the RhCl_3 solution is added,
- triphenylphosphin is added in excess as an alcoholic suspension,
- 10 **A** the suspension obtained in an initial stage is heated up from about 20 to about 25 to 30°C,
- B** further in a second stage is heated up from about 25 to 30 to about 75°C,
- C** is boiled under reflux at 80 to 110°C,
- the solution obtained is cooled down,
- 15 - the crystals precipitated out are filtered, washed with alcohol and/or water and/or petroleum ether and subsequently dried.

An advantage of the embodiment of the technique is that the overall synthesis can transpire within a single day if, as in Embodiment 4, the reaction is started at room
20 temperature, without preliminary cooling down of the solvent. This in practice proves to be a substantial economic advantage.

Even with the processing it has proven to be advantageous after Stage **C** actively to cool down the solution. Surprisingly this does not have any unfavorable impact on the
25 crystal size and provides a great advantage by the saving of time in relation to the energy expended for cooling down.

Furthermore, it is possible to achieve an improved space-time yield by limiting the solvent quantity, as described in Example 5. With this procedure smaller crystals that
30 may potentially arise can be filtered by means of a pressure filter so that with production of larger quantities overall a very economical technique results.

Furthermore, the crystalline product's drying process can be tweaked to the effect that washing can be done with isopropanol and if need be petroleum benzine. Thus on an industrial scale drying times of only a day are possible.

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The following examples serve as illustration of the invention without limiting it. Yields are given in% relating to rhodium used.

Examples: Comparative Example: State of the Art, Wilkinson's Rule

- 10 Synthesis according to Inorg. Synth **10**, 67 (1967) and identically Inorg. Synth **28**, 77 (1990)

In a 500 ml round-bottomed flask with gas intake pipe, reflux condenser and gas outtake 2 g rhodium(III)-chloride-trihydrate are dissolved in 70 ml ethanol. A solution of 12 g triphenylphosphin freshly recrystallized from EtOH is added in 350 ml hot
15 ethanol and the flask is rinsed with nitrogen. The solution is boiled at reflux for two hours and the crystalline product is filtered out of the hot solution on a frit. After washing with small portions of 50 ml water-free ethanol 6.25 g is obtained (yield: 88% relating to Rh).

- 20 Example 1: Wilkinson's Rule with Inventive Temperature Control Stage B and C

Apparatuses 1 and 2: Round-bottomed flask with gas intake, reflux cooler and gas outtake.

- 25 In apparatus 2, 24g (0.0916 mole) triphenylphosphin under argon are produced and dissolved in 700 ml ethanol. At 40°C the entire triphenylphosphin has already dissolved.

In apparatus 1 in the meantime, 4 g (0.0158 mole) RhCl_3 hydrate is produced and
30 suspended in 140 ml ethanol. To the reddish brown suspension is now added under argon intake flow the triphenylphosphin solution warmed to 40°C. A deep red solution arises with a temperature of 36°C. The solution is now slowly heated to simmering.

	<u>Temperature:</u>	<u>Processing Time:</u>	<u>Observation:</u>
	36 – 62°C	55 min	orange suspension
	62 – 67°C	25 min	suspension becomes gradually darker and changes colors through brown to wine red
5	67°C		reaction occurred; a dark ruby-colored suspension has arisen (change point)
	67 – 79°C	70 min	dark ruby-colored suspension
	79 – 80°C		start simmering; suspension is boiled 2 h on reflux

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The suspension obtained is cooled down by means of an ice bed to 20°C and subsequently filtered through a G3 frit. The ruby-colored product is rewashed on the frit 2 x with 50 ml ethanol each and dried in the vacuum of membrane pumps. 14,549 g of ruby-colored solid were obtained. The calculated yield amounts to 99.2%.

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Example 2

4 g Rh (0.0389 mole) in form of an aqueous RhCl_3 solution with 23% rhodium content are dissolved under argon in 490 ml isopropanol in a round-bottomed flask with gas intake and outtake cooler and cooled down to 5°C by means an ice bath.

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With this temperature under stirring 50 g (0.191 mole) triphenylphosphin is added in and subsequently slowly heated up to simmering.

25	<u>Temperature:</u>	<u>Processing Time:</u>	<u>Observation:</u>
	5°C		dark reddish brown solution with undissolved triphenylphosphin
	10 – 31°C	1 h	brown suspension
	25 – 70°C	3.25 h	orange suspension

	70 – 75°C	30 min	suspension becomes gradually darker and changes colors via brown to ruby-colored
	75°C		reaction occurred; a dark ruby-colored suspension has arisen (change point)
5	75 – 79°C	15 min	ruby-colored suspension
	79 – 80°C		simmering starts; suspension is boiled for 1 h on reflux

The suspension obtained is left to cool down over night without active cooling. On the following day cooling down to 10°C by means of an ice bath takes place and subsequently filtering over a G3 frit. The product is rewashed on the frit with 235 ml isopropanol and 100 ml petroleum benzine and dried in the vacuum of membrane pumps.

35.81 g (0.0387 mole) of ruby-colored solid are obtained.

The calculated yield amounts to 99.4%.

Example 3

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One day prior to the actual synthesis 4 g Rh (0.0389 mole) in form of an RhCl_3 hydrate (Rh content 40.7%) is dissolved in 26 ml of totally desalinated water overnight. In a round-bottomed flask with gas intake and outtake cooler as well as reflux cooler 490 ml isopropanol are produced under argon. The RhCl_3 solution is added in. Then 50 g (0.191 mole) triphenyl-phosphine are added and subsequently the suspension is heated up to simmering.

	<u>Temperature:</u>	<u>Processing Time:</u>	<u>Observation:</u>
	21°C		brown suspension
30	25 – 70°C	4 h	orange suspension
	70 – 75°C	40 min	suspension becomes gradually darker and changes colors through brown to ruby-colored

	75°C		reaction occurred; a dark ruby-colored suspension has arisen (change point)
	75 – 79°C	25 min	ruby-colored suspension
	79 – 80°C		simmering starts; suspension is boiled for 1 h on reflux

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The suspension obtained is left to cool down over night without active cooling. On the following day cooling down to 20°C by means of an ice bath takes place and subsequently filtering over a G3 frit. The product is rewashed on the frit with 405 ml of totally desalinated water and 235 ml isopropanol. Subsequently the frit cake is dried in the vacuum of membrane pumps. 35.82 g of ruby-colored fine crystalline solid are obtained.

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The calculated yield amounts to 99.4%.

Example 4

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4 g Rh (0.0389 mole) in form of an aqueous RhCl_3 solution with 23% Rh content is thinned with water to an Rh content of 10%.

490 ml isopropanol are mixed with the RhCl_3 solution. Then 50 g (0.191 mole) of triphenylphosphin is introduced into the flask and heated up to simmering in stages.

	<u>Temperature:</u>	<u>Processing Time:</u>	<u>Observation:</u>
25	19°C		dark reddish brown solution with un-dissolved triphenylphosphin
	25 – 30°C	30 min	brown suspension
	30 – 74°C	3.25 h	orange suspension
	74 – 78°C	30 min	suspension becomes gradually darker and changes colors via brown to ruby-colored
30	78°C		reaction occurred; a dark ruby-colored

suspension has arisen (change point)

78 – 79°C 15 min

ruby-colored suspension

79 – 80°C

simmering starts; suspension is boiled for 1 h on
reflux

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The suspension obtained is cooled down to 20°C by means of an ice bath and subsequently filtered over a G3 frit. The product is rewashed on the frit with 235 ml isopropanol and 100 ml of petroleum benzine and dried in the vacuum of membrane pumps.

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35.47 g of ruby-colored fine crystalline solid are obtained.

The calculated yield amounts to 98.5%.

15 Example 5

(Repeat of Example 4 but with 30% less solvent and water)

343 ml isopropanol and 4 g Rh in form of an RhCl_3 solution with an Rh content of 10% are produced along with the triphenylphosphin are produced in the flask and similar to Example 4 heated to simmering in stages.

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Temperature: Processing Time: Observation:

19°C

dark reddish brown solution with un-dissolved triphenylphosphin

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26 – 34°C

45 min

brown suspension

34 – 68°C

3 h

orange suspension

68 – 75°C

45 min

suspension becomes gradually darker

and changes colors via brown to ruby-colored

75°C

reaction occurred; a dark ruby-colored

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suspension has arisen (change point)

75 – 79°C

15 min

ruby-colored suspension

79 – 80°C

simmering starts; suspension is boiled for 1 h on
reflux

The suspension obtained is cooled down to 20°C by means of an ice bath and subsequently filtered over a G3 frit. The product is rewashed on the frit with 235 ml isopropanol and 100 ml of petroleum benzine and dried in the vacuum of membrane pumps.

34.44 g of ruby-colored fine crystalline solid are obtained.

The calculated yield amounts to 95%.